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PATENT SPECIFICATION

761,327



Date of Application and filing Complete Specification:
Nov. 11, 1954.

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COMPLETE SPECIFICATION

**Process for the Polymerisation or Copolymerisation of
Polymerisable Fluorine-containing Compounds**

PATENTS ACT, 1949

SPECIFICATION NO. 761,327

Reference has been directed, in pursuance of Section 8, of the Patents Act, 1949, to Specification No. 767,757.

THE PATENT OFFICE,
2nd July, 1958

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Block polymerisation has various disadvantages. For example, it is difficult to control the reaction in such a manner that uniform products are obtained at high conversions, and it is often necessary to interrupt the polymerisation prematurely with the result that the conversion is low.

Attempts have been made to carry out the polymerisation in a solvent for chloro-trifluorethylene. However, it is very difficult to obtain products of high molecular weight by this process, since many solvents have a chain-breaking effect and are also unavoidably and undesirably incorporated in the product. The removal of the last traces of solvent from the product is a costly and time-consuming operation, but it is necessary because even small amounts of solvent in the product give rise to discoloration in the moulded sheet.

Products of high molecular weight can be obtained at high conversions per unit of time and volume when working in the aqueous phase, especially with the use of a Redox catalyst system. The process may be a suspension polymerisation process without the use of an emulsifier (in which the particles of polymer formed precipitate) or an emulsion polymerisation with the use

emulsion system to produce a wetted product, but the usual emulsifiers either inhibit the polymerisation completely or lead to low conversions.

It is known that the polymerisation of the chloro-trifluorethylene can be carried out with satisfactory yields in the presence of emulsifiers of the type of polyfluorocarboxylic acids, acid sulphuric or phosphoric acid esters of polyfluoralkylhydroalcohols or salts of polyfluoralkylamines. However, these emulsifiers are difficult to prepare, they necessitate costly apparatus, especially in the first stage of their preparation, and they lead to only moderate yields of the product.

The present invention provides a process for polymerising a polymerisable fluorine-containing organic compound dispersed in an aqueous medium alone or jointly with another such fluorine-containing compound or other copolymerisable compound, wherein the polymerisation is conducted in the presence of a chloro-fluoro-carboxylic acid with at least 5 carbon atoms or a salt thereof as dispersing agent. The chlorofluorocarboxylic acids can be rapidly and smoothly prepared, for example, by the oxidation with permanganate in a weakly alkaline medium of a chlorofluorocarbon oil, for

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COMPLETE SPECIFICATION

Process for the Polymerisation or Copolymerisation of Polymerisable Fluorine-containing Compounds

We, FARBWERKE HOECHST AKTI-
ENGESSELLSCHAFT vormals Meister
Lucius & Brüning, a body corporate recog-
nised under German law, of Frankfurt
5 (M)-Höchst, Germany, do hereby declare
the invention, for which we pray that a
patent may be granted to us, and the
method by which it is to be performed, to
be particularly described in and by the
10 following statement:—

Various processes are known for poly-
merising chloro-trifluorethylene to produce
valuable artificial plastics of high molecular
weight. These processes may be carried out
15 as a so-called block polymerisation or in an
organic solvent or in water.

Block polymerisation has various disad-
vantages. For example, it is difficult to
control the reaction in such a manner that
20 uniform products are obtained at high con-
versions, and it is often necessary to inter-
rupt the polymerisation prematurely with
the result that the conversion is low.

Attempts have been made to carry out
25 the polymerisation in a solvent for chloro-
trifluorethylene. However, it is very difficult
to obtain products of high molecular weight
by this process, since many solvents have a
chain-breaking effect and are also unavoid-
30 ably and undesirably incorporated in the
product. The removal of the last traces of
solvent from the product is a costly and
time-consuming operation, but it is necessary
because even small amounts of solvent in
35 the product give rise to discoloration in the
moulded sheet.

Products of high molecular weight can
be obtained at high conversions per unit of
time and volume when working in the aque-
ous phase, especially with the use of a
40 Redox catalyst system. The process may
be a suspension polymerisation process
without the use of an emulsifier (in which
the particles of polymer formed precipitate)
45 or an emulsion polymerisation with the use

of an emulsifier (in which the particles of
polymer formed do not precipitate).

The suspension polymerisation of chloro-
trifluorethylene has the disadvantage that
the greater part of the polymer produced 50
is completely unwetted. Moreover, since
the polymer contains adsorbed salts which
produce discoloration during moulding, it is
necessary to clean the polychlorotrifluor-
ethylene powder by washing, and this is a 55
time-consuming and costly operation, since
the unwetted powder cannot be cleaned by
simple filtration and washing.

Attempts have therefore been made to
polymerise chloro-trifluorethylene in an
emulsion system to produce a wetted prod- 60
uct, but the usual emulsifiers either inhibit
the polymerisation completely or lead to
low conversions.

It is known that the polymerisation of 65
the chloro-trifluorethylene can be carried
out with satisfactory yields in the presence
of emulsifiers of the type of polyfluoro-
carboxylic acids, acid sulphuric or phos-
phoric acid esters of polyfluoralkyl- 70
hydroalcohols or salts of polyfluoralkyl-
amines. However, these emulsifiers are
difficult to prepare, they necessitate costly
apparatus, especially in the first stage of
their preparation, and they lead to only 75
moderate yields of the product.

The present invention provides a process
for polymerising a polymerisable fluorine-
containing organic compound dispersed in
an aqueous medium alone or jointly with 80
another such fluorine-containing compound
or other copolymerisable compound, where-
in the polymerisation is conducted in the
presence of a chloro-fluoro-carboxylic acid
with at least 5 carbon atoms or a salt there- 85
of as dispersing agent. The chlorofluoro-
carboxylic acids can be rapidly and smoothly
prepared, for example, by the oxidation
with permanganate in a weakly alkaline
medium of a chlorofluorocarbon oil, for 90

example, the fraction having a boiling range of 30°C. to 170°C. under a pressure of 5 mm of mercury, obtained by cracking polychlorotrifluoro-ethylene, or a copolymer derived mainly from chlorotrifluoroethylene, in the presence of copper sulphate. The chloro-fluoro-carboxylic acids used in the present process contained a chain of at least 5 carbon atoms which may be branched. Advantageously, the chain contains about 5 to 20 carbon atoms. The acids may also be prepared in the manner described in British Patent Application No. 25,025/54 (Serial No. 758,419).

This type of emulsifier is especially advantageous because the alkyl residue attached to the carboxyl group is composed of chloro-trifluoroethylene units ($-\text{CF}_2-\text{CFCl}-$), so that the emulsifier is similar in structure to the monomer being polymerised and is compatible therewith.

Stable dispersions are produced by the addition of about 0.5 to about 30 per cent, and preferably 0.5 to about 10 per cent, by weight of the chloro-fluoro-carboxylic acid based on the weight of monomer used. These stable dispersions must be precipitated in order to transform them by a further treatment into solid substances. Unstable dispersions which settle out or are filterable can be obtained by using the chloro-fluoro-carboxylic acid in a proportion ranging from about 0.05 to about 0.5 per cent by weight, and preferably about 0.1 to about 0.5 per cent by weight, based on the weight of monomer used. The latter procedure is especially advantageous in practice. The adsorbed emulsifier and other materials used in the polymerisation can be removed from the polymer practically quantitatively by simple washing.

As compared with the polyfluorocarboxylic acids and similar known emulsifiers, the use of the chloro-fluoro-carboxylic acids avoids the need of first preparing the alkali metal or ammonium salts of the acids, since the free chloro-fluoro-carboxylic acids are clearly soluble in the aqueous phase of the polymerisation system. Since the acids are produced as free acids, and since the preparation of alkali metal salts thereof involves certain difficulties due to the high solubility in water of the salts, the fact that the chloro-fluoro-carboxylic acids can be used as such in the polymerisation constitutes an additional advantage of this emulsion process.

Further advantages arising from the use of chloro-fluoro-carboxylic acids as emulsifiers in the polymerisation or copolymerisation of chloro-trifluoroethylene, as distinguished from other emulsifiers, are the increase speed of polymerisation and the greatly increased bulk density of the polymers produced in this manner.

Moreover, since, as stated above, there

can be obtained by the use of chloro-fluoro-carboxylic acids stable dispersions in which the polymer is present in a very finely divided state (by the use of 0.5 to 30 per cent of a chloro-fluoro-carboxylic acid in colloidal state, see above) the latices so obtained can be filtered by means of conventional filters. This has the advantage that contaminants or foreign materials, which cannot be removed from the product after precipitation of the latices, can be removed by simple filtration before working up the product.

The process is especially useful for the polymerisation or copolymerisation of chloro-trifluoroethylene. Among the polymerisable components suitable for copolymerisation there may be mentioned, for example, tetrafluoroethylene, vinylidene fluoride, trifluoropropylene, 1:1-dichloro-2:2-difluoroethylene, 1:2-dichloro-1:2-difluoroethylene, vinyl fluoride, trifluoroethylene, vinyl chloride and vinylidene chloride. Other copolymerisable monomers include halogen-free vinyl compounds, such as the esters of methacrylic acid and acrylic acid, vinyl acetate, vinyl propionate.

Other fluorine-containing monomers, for instance, tetrafluoroethylene, trifluoroethylene, vinylidene fluoride or vinyl fluoride can be polymerised by the process of this invention.

The emulsion polymerisation process of the invention may be carried out at temperatures within the range of about 0°C to about 100°C., and preferably at temperatures within the range of about 5°C to about 70°C. Superatmospheric pressures within the range of about 1 atmosphere gauge pressure to the saturation pressure at the desired temperature may be used, if desired; and it may sometimes be advantageous to use pressures higher than the saturation pressure of the monomeric components by the introduction of an inert gas, such as nitrogen, under superatmospheric pressure or by the application of liquid pressure. The pressure may be within the range of about 1 to about 50 atmospheres, and preferably about 3 to about 20 atmospheres, gauge pressure.

As initiators for the polymerisation reaction there may be used inorganic or organic peroxides or peroxy-acids or their salts, and alkali metal salts of peroxydisulphuric acids have been found especially useful.

Redox catalyst systems may also be used in which, in addition to one of the above oxidising agents, there is added a water-soluble reducing agent, such as a sulphite, a bisulphite, an alkali metal salt of formaldehyde-sulphoxylic acid, a dithionite and/or a salt of a metal having more than one

valency, such as iron, cobalt, copper, nickel or the like. It is sometimes desirable to maintain the pH value of the reaction mixture constant during the polymerisation, and for this purpose buffers such as phosphates, borax or acetates may be added.

Stable dispersions containing the higher proportions of chloro-fluoro-carboxylic acid emulsifiers may be used, *inter alia*, for impregnating porous materials and for the production of coatings. The polymers obtained by the process of the invention are especially useful for the preparation of dispersions of polymers in organic solvents, such as esters of glycolic acid with, for example, butanol; ketones, such as acetone or methyl ethyl ketone; alcohols, such as amyl alcohol; and hydrocarbons such as mesitylene. It will be understood that also the other known dispersing media for these substances of high molecular weight may be used.

The following Examples illustrate the invention, the parts and percentages being by weight:

Example 1

A rocking autoclave of stainless steel was carefully exhausted of oxygen by repeated evacuation and filling with nitrogen gas under pressure, and was then charged with 2700 parts of an aqueous medium containing 50 parts of secondary sodium phosphate, 10 parts of sodium bisulphite and 6.4 parts of a chloro-fluoro-carboxylic acid (prepared by the oxidation of a chlorofluorocarbon oil fraction having a boiling range of 170°C to 230°C. under a pressure of 5 mm of mercury) in distilled water which had been boiled under nitrogen.

1000 parts of chloro-trifluorethylene were then added under nitrogen gas pressure, after evacuation of the autoclave. During the polymerisation the temperature was maintained at 30°C., which produced 7.4 atmospheres gauge pressure. The autoclave was rocked, and there were added in the course of 15 minutes 300 parts of a solution of 15 parts of potassium persulphate in distilled water, which had been boiled under nitrogen.

After the polymerisation had proceeded for 5 hours the pressure had fallen to 5 atmospheres gauge pressure. There were obtained 780 parts of a completely wetted polymer in the form of a paste, which was then filtered and washed. The polymer was still in the wetted condition after the washing. The product had an N.S.T. value of 300, and the mechanical and thermal properties thereof were the same as those of a product prepared in the absence of a chloro-fluoro-carboxylic acid emulsifier.

Example 2

A stainless steel rocking autoclave was carefully exhausted of oxygen by repeated

and filling with nitrogen gas under pressure, and was then charged with 1000 parts of an aqueous liquor containing 3.0 parts of secondary sodium acetate, 1.4 parts of potassium persulphate, 1 part of sodium bisulphite and 5.0 parts of a chloro-fluoro-carboxylic acid (prepared by the oxidation of a fluorochlorocarbon oil fraction boiling at 170°C to 230°C. under a pressure of 5 mm of mercury) in distilled water, which had been boiled under nitrogen. 335 parts of chloro-trifluorethylene were then added under nitrogen gas pressure, after evacuating the autoclave. The polymerisation was conducted at a temperature of 30°C, which produced 7.4 atmospheres gauge pressure. After a period of 4 hours, the pressure had fallen to 6.5 atmospheres gauge.

There was obtained a stable dispersion having a solid content of 20 per cent and a slightly bluish colour. Since this dispersion was not filterable, it was precipitated hot with 500 parts of concentrated sodium chloride solution. The polymer was then filtered off and washed with 8000 parts of hot distilled water until free from chloride. 191 parts of a polymer having an N.S.T. value of 300 were obtained. The polymer remained wetted even after repeated washing, and had mechanical and thermal properties equivalent to those of a polymer prepared in the absence of a chloro-fluoro-carboxylic acid emulsifier.

Example 3

Following the procedure described in Example 1, a rocking autoclave was charged with an aqueous liquor consisting of 30 parts of secondary sodium phosphate, 5 parts of sodium bisulphite, 6 parts of a chloro-fluoro-carboxylic acid (prepared by the oxidation of a chlorofluorocarbon oil fraction boiling at 30°C to 170°C. under a pressure of 5 mm of mercury) and 2659 parts of distilled water, which had been boiled under nitrogen.

After evacuating the autoclave, 1000 parts of a mixture of 90 per cent of chloro-trifluorethylene and 10 per cent of vinylidene fluoride were added under nitrogen gas pressure. The polymerisation was conducted at a temperature of 30°C., which produced an autogenous pressure of 9.5 atmospheres gauge. There were then added in the course of 15 minutes 300 parts of a solution of 6.7 parts of potassium persulphate and 0.078 part of copper sulphate in distilled water, which had been boiled under nitrogen.

After 55 minutes the pressure had fallen to 7.3 atmospheres gauge. A latex was obtained which, after dilution with 5000 parts of distilled water, was precipitated hot by being boiled with 700 parts of a solution of 20 per cent strength of sodium chloride. 890 parts of a copolymer were obtained by centrifuging, washing with hot distilled

water, and drying.

The copolymer had a bulk density of 0.8 grams per cc., an N.S.T. value of 314 and a specific viscosity of 2.6 determined in a solution of 1 per cent strength in 2:5-dichlorobenzotrifluoride at 130°C. The copolymer had a tensile strength of 290 kg/sq.cm., a breaking elongation of 250 per cent and Shore Hardness of D:65.

Example 4

The procedure of Example 3 was repeated using a mixture of monomers consisting of 90 per cent of chloro-trifluorethylene and 10 per cent of vinylidene fluoride. The reaction conditions were the same as in Example 3, except that the polymerisation temperature was maintained at 5°C. 950 parts of a copolymer were obtained after polymerising for 18 hours. The copolymer had a bulk density of 0.8 grams per cc, an N.S.T. value of 316 and a specific viscosity of 7.7 (as determined in Example 3).

Example 5

The procedure of Example 3 was repeated, except that the quantities of bisulphite and potassium persulphate were reduced to one-fifth of those used in Example 3. The same mixture of chloro-trifluorethylene and vinylidene fluoride was used. The polymerisation was conducted at 30°C. for a period of 4 hours, and 790 parts of a copolymer were obtained. The copolymer had an N.S.T. value of 336 and specific viscosity of 27 (see above).

Example 6

The procedure of Example 3 above was repeated, except that the quantities of bisulphite and potassium persulphate were reduced to one-tenth of those used in Example 3. The same mixture of monomers was copolymerised at 30°C under the conditions described in Example 3, and after 5 hours and interruption without pressure drop there were obtained 870 parts of a copolymer having a specific viscosity of 21.

This procedure was repeated in the absence of a chloro-fluoro-carboxylic acid emulsifier, and 190 parts of a copolymer having a specific viscosity of 15 were obtained after copolymerising the monomers for 24 hours.

Example 7

The procedure of Example 1 above was repeated using a rocking autoclave charged with 3000 parts of an aqueous liquor consisting of 50 parts of secondary sodium phosphate, 0.5 part of sodium bisulphite, 0.67 part of potassium persulphate, 0.078 part of copper sulphate and 6 parts of a chloro-fluoro-carboxylic acid (prepared by the oxidation of a chlorofluorocarbon oil fraction boiling at 30°C to 170°C. under a pressure of 5 mm of mercury) in distilled water which had been boiled under nitrogen. After evacuating the autoclave, 1000

parts of a mixture of 95 per cent chloro-trifluorethylene and 5 per cent of vinylidene fluoride were added under nitrogen gas pressure. The polymerisation temperature was maintained at 30°C, which produced an autogenous pressure of 8.5 atmospheres gauge. After copolymerising for 20 hours, the pressure had fallen to 8 atmospheres gauge. 580 parts of a copolymer having a specific viscosity of 16 were obtained, after dilution and precipitation of the product with hot sodium chloride solution.

This procedure was repeated using the same mixture of monomers, except that no chloro-fluoro-carboxylic acid was added. 130 parts of a copolymer having a specific viscosity of 10 were obtained, after copolymerising the monomers for 24 hours and interruption without pressure drop.

Example 8

The procedure of Example 1 above was repeated, the rocking autoclave being charged with 3000 parts of an aqueous liquor containing 50 parts of secondary sodium phosphate, 5 parts of sodium bisulphite, 6.7 parts of potassium persulphate, 0.078 part of copper sulphate and 6 parts of a chloro-fluoro-carboxylic acid (prepared by the oxidation of a chlorofluorocarbon oil fraction boiling at 30°C. to 170°C. under a pressure of 5 mm of mercury). After evacuation, 1000 parts of a mixture of 98 per cent of chlorotrifluorethylene and 2 per cent of vinylidene fluoride were added under nitrogen gas pressure. The polymerisation temperature was maintained at 30°C. producing an autogenous pressure of 7.6 atmospheres gauge. After 4.25 hours the pressure had fallen to 6 atmospheres gauge.

880 parts of a copolymer having an N.S.T. value of 317 and a specific viscosity of 1.5 were obtained. The copolymer had a tensile strength of 321 kg/sq.cm., a breaking elongation of 94 per cent and a Shore Hardness of D:72.

A strip of the copolymer 1.6 mm in thickness did not break when bent over a mandrel through an angle of 180° and kept at a temperature of 190°C for 80 days.

Example 9

The procedure of Example 8 was repeated using a mixture of monomers consisting of 970 parts of chloro-trifluorethylene and 30 parts of 1:1:1-trifluoropropylene. The polymerisation was conducted at 30°C. for 3 hours, and the product was obtained at a conversion of 85 per cent based upon the weight of monomers used. The polymer had an N.S.T. value of 297, and did not fail in the bending test described in Example 8 above after 27 days.

Example 10

Following the procedure of Example 8, an identical aqueous liquor was charged into a silver-lined autoclave provided with

- stirring means, and a mixture of 650 parts of chloro-trifluorethylene and 350 parts of vinylidene fluoride was then added. After copolymerising the monomers for 1.25 hours, a copolymer was obtained at a conversion of 75 per cent based on the weight of monomers used. The copolymer had a breaking elongation of 300 to 500 per cent and a tensile strength of 100 kg/sq.cm. Its Shore Hardness D was between 20 and 30.
- A rubber-like sheet produced from the product by vulcanisation with dibenzoyl peroxide and zinc oxide exhibited good elastomeric properties.
- 15 What we claim is:
1. A process for polymerising a polymerisable fluorine-containing organic compound dispersed in an aqueous medium alone or jointly with another such fluorine-containing compound or other copolymerisable compound, wherein the polymerisation is conducted in the presence of a chloro-fluoro-carboxylic acid containing a chain of at least 5 carbon atoms or a salt thereof as dispersing agent.
 2. A process as claimed in claim 1, wherein the chloro-fluoro-carboxylic acid or salt thereof contains a chain of at least 5 carbon atoms.
 - 30 3. A process as claimed in claim 1, wherein the chloro-fluoro-carboxylic acid or salt thereof contains a chain of 5 to 20 carbon atoms.
 4. A process as claimed in claim 1, 2 or 3, wherein the proportion of the said emulsifying agent is within the range of about 0.05 to 30.0 per cent or the weight of the polymerisable compound or compounds.
 5. A process as claimed in claim 4, wherein the said proportion is within the range of about 0.5 to 30.0 per cent.
 6. A process as claimed in claim 5, wherein the said proportion is within the range of about 0.5 to 10.0 per cent.
 7. A process as claimed in claim 4, wherein the said proportion is within the range of about 0.05 to 0.5 per cent.
 8. A process as claimed in any one of claims 1-7, wherein the polymerisable fluorine-containing compound is an ethylenically unsaturated compound containing at least one fluorine atom bound to the carbon atom of an ethylenic linkage.
 9. A process as claimed in claim 8, wherein the fluorine-containing compound is chloro-trifluorethylene.
 10. A process as claimed in claim 8, wherein the fluorine-containing compound is tetrafluorethylene, trifluorethylene, vinylidene fluoride or vinyl fluoride.
 11. A process as claimed in any one of claims 1-7, wherein chloro-trifluorethylene is polymerised with another polymerisable compound.
 12. A polymerisation process conducted substantially as described in any one of Examples 1-5, 8, 9 and 10 and in the first paragraph of Examples 6 and 7 herein.
 13. A polymer or copolymer whenever obtained by the process claimed in any one of claims 1-12.

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